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Cite as:
Agatemor, C., Arnold, A. E., Cross, E. D., Decken, A., & Shaver, M. P. (2013). Aluminium salophen and salen initiators in the ring-opening polymerisation of rac-lactide and rac-β-butyrolactone: Electronic effects on stereoselectivity and polymerisation rates. *Journal of Organometallic Chemistry*, 745-746, 335-340.

Manuscript received: 27/06/2013; Accepted: 12/08/2013; Article published: 21/08/2013

Aluminium Salophen and Salen Initiators in the Ring-opening Polymerisation of *rac*-Lactide and *rac*-*β*-Butyrolactone: Electronic Effects on Stereoselectivity and Polymerisation Rates**

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[**]The financial support of the Natural Sciences and Engineering Research Council of Canada, the Canada Foundation for Innovation, the Atlantic Canada Opportunities Agency and the Universities of Prince Edward Island and Edinburgh is acknowledged. We also thank Professor Rabin Bissessur for DSC analyses, Dr. Laura Allan for GPC analyses, Dr. Fabrice Berrue and Patricia Boland for ESI-MS analyses and Mr. Stephen Scully for NMR analyses.

Supporting information:
Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.08.023

Highlights:
Four new aluminium salen and salophen complexes; Electronic variation of ligand backbone; Changes in polymerisation rates and tacticity in lactide and beta-butyrolactone polymerisation.

Keywords:
Salen; Salophen; Poly(lactic acid); Poly(3-hydroxybutyrate); *rac*-Lactide; *rac*-*β*-Butyrolactone

Abstract

Three aluminium salophen and two aluminium salen complexes were synthesised, characterised and screened in the ring-opening polymerisation (ROP) of *rac*-lactide and *rac-β*-butyrolactone. The focus was on controlling the apparent polymerisation rate (k_p) and stereoselectivity of poly(lactic acid) and poly(3-hydroxybutyrate) by modulating the electron density at the aluminium centre or by switching from an alkyl backbone (salen complex) to an aryl backbone (salophen complex). The salen complexes generally showed higher k_p as well as isoselectivity compared to the salophen complexes. For instance, salophen and salen complexes biased the microstructure of poly(3-hydroxybutyrate) towards syndiotacticity and isotacticity, respectively. Electron-withdrawing or electron-donating backbones on a salophen complex tuned k_p, with electron-donating backbones offering faster k_p.

1. Introduction

Ring-opening polymerisation (ROP) is the most efficient synthetic approach to aliphatic polyesters, a class of biodegradable, often renewable, and commercially relevant materials. Unlike condensation polymerisation, ROP yields polymers with predictable and controllable molecular weights and polydispersities (Đ) [1]. Significant effort in designing efficient organo- and organometallic-based complexes as catalysts for the ROP of cyclic esters has led to increased reaction rates, improved monomer scope and tacticity control [2]. While organo complexes offer many attractive features for metal-free commodity production of these materials [2a], organometallic complexes remain competitive due to low catalyst loadings, high tacticity control and a coordination framework that can be tailored to a particular product or application [2d,3,4].

The supporting ligand in the organometallic complex is crucial to the overall performance of these catalysts. Methodical variation of the ligand structure can often modulate the performance of the complex in ROP over a broad range. In salen and salophen ligands, the substituents on the phenoxy group and the backbone can significantly influence the rate and stereoselectivity of the polymerisation reaction [2p], as is the case for mixed salen/salan "salalen" frameworks [5]. For instance, electron-withdrawing substituents on the phenoxy group of aluminium salen complexes have been reported to increase polymerisation rate while bulky groups concurrently decreased the rate and increased isospecificity [2p].

Recently, we reported a designed aluminium salen complex (**1**) (Figure 1) where a bulky adamantyl group on the phenoxy group improves isotacticity of PLAs compared with a *tert*-butyl substituted phenoxy group whilst also reporting an increased monomer scope and robust immortal polymerisation conditions [2k]. We were inspired by the recent work of Rieger *et al.* on electronic effects in chromium salophen complexes mediating ROP reactions [2l] to extend this investigation to adamantyl salophen derivatives and their role in the aluminium mediated ROP of *rac*-lactide and *rac-β*-butyrolactone.

Herein, four novel aluminium complexes are prepared (Figure 1, **2**-**5**), three of which contain a conjugated aryl backbone with different electronic substitutions on the phenylene group. Synthesis, characterisation and polymerisation screening in the ROP of *rac*-*β*-butyrolactone (*rac*-*β*BL) and *rac*-lactide (*rac*-LA) were performed, with a particular focus on investigating the effects of electron donation and withdrawal from the backbone into the aluminium centre as well as the effect of alkyl vs. aryl backbone on both the apparent polymerisation rate (k_p) and stereoselectivity of ROP. Although the effect of ligand electronics on the polymerisation rate is well reported [2l,o-q,6], interest in this field continues to provide insight into mechanism, especially in instances of conflicting electronic trends. To the best of our knowledge, this submission also represents the first report of aluminium salophen complexes in the ROP of multiple cyclic esters.

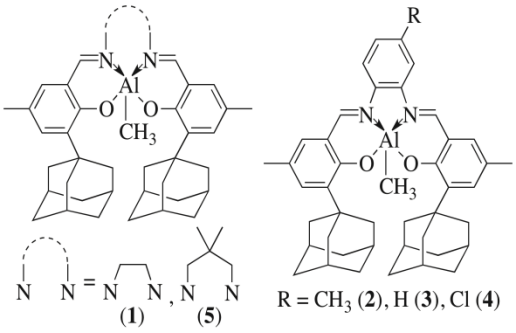


Figure 1. Salophen (**2**-**4**) and salen (**1**,**5**) aluminium pre-catalysts.

2. Results and discussion

A well-established condensation of the adamantyl-substituted salicylaldehydes and the appropriate diamine afforded the desired ligand frameworks. Subsequent protonolysis of the proligand with trimethylaluminium at 110 ˚C for 12 h afforded the desired complexes **2**-**5**. ^{1}H and ^{13}C NMR spectroscopy along with elemental analyses confirmed the nature and purity of the catalysts. The molecular structure of **5** (Figure 2) was determined from the X-ray diffraction of a single crystal grown by slow evaporation from toluene solution to further support the assignment of a mononuclear, penta-coordinate structure that featured a distorted trigonal bipyramidal geometry at the aluminium centre. The pronounced twist in the backbone, aided by the isopentyl bridge, induces an increased asymmetry in phenoxide bonds when compared to the structure of **1**, with Al-O distances differing by 0.05 Å in **5** compared to 0.01 Å in **1** [2k]. Solution ^{1}H NMR structure characterisation showed notable differences in the splitting pattern of the imine protons of the initiators. **3** and **5** featured a singlet resonance (δ 7.89 ppm, **3**; 7.39 ppm, **5**) suggesting a symmetric structure for these compounds while complex **2** had resonances at δ = 7.90 and 7.94 ppm and **4** had two singlet resonances at δ = 7.74 ppm and 7.57 ppm suggesting non-equivalence of the two imine protons. The asymmetry induced by the broken symmetry of the backbone is stronger for the sterically and electronically more directing halogen substituent, as expected.

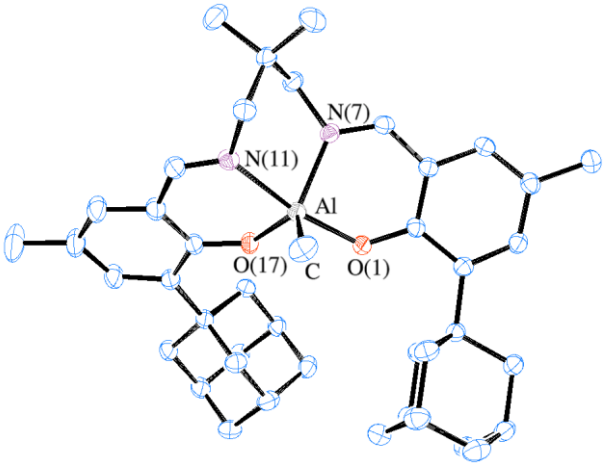
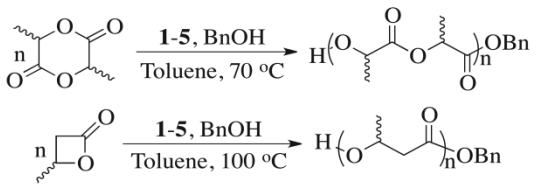


Figure 2. Molecular structure of initiator **5** with thermal ellipsoids drawn at the 50% probability level. Hydrogen and solvent atoms omitted for clarity. Selected bond lengths (Å): Al-O(1), 1.8496(12); Al-O(17), 1.8032(12); Al-C, 1.9804(19); Al-N(7), 2.0200(14); Al-N(11), 2.0577(14). Deposited as CCDC 940611.

These initiators were screened in the ROP of *rac*-LA and *rac*-*β*BL (Scheme 1). *In-situ* conversion to the active aluminium benzoxide complex was achieved by the addition of an equivalent of benzyl alcohol prior to monomer addition. Importantly, no polymerisation was observed directly from the Al-CH_3 bond on these polymerisation timescales. Aluminium alkoxides were not isolated and separately screened as we wished to compare to existing salen data on alkyl complexes [2p] and expected little differences in activity from immortal-type catalysts with rapid alcohol exchange [2k]. Electrospray ionisation mass spectrometry (ESI-MS) was used to ascertain the role of the complexes in the polymerisation. Low-molecular weight oligomers (ca 4000 Da) were synthesised and analysed by ESI-MS to determine the size of repeating units and benzoxide end-groups [7]. ESI-MS spectra confirm the formation of aluminium-benzoxide complex as peaks that correspond to masses of the benzoxide end group, sodium adduct, and a degree of polymerisation were apparent (Electronic Supplementary Material, Figure S1). While no methyl-terminated polymer chain was observed, small peaks indicative of some trans-esterification were also noted in the spectra, suggesting polymer chain backbiting would be responsible for increases in polydispersities.



Scheme 1. Polymerisation of *rac*-LA and *rac*-*β*BL by **1-5**.

Molecular weight characteristics of the resulting polymers were determined by gel permeation chromatography (Table 1). Control over both the ROP of *rac*-lactide and *rac-β*BL was improved for alkyl-backbone complexes **1** and **5**, including lower Đ and predictable molecular weights. As previously observed [2k], polymerisation of *rac-β*BL appeared to proceed much faster than corresponding *rac*-LA polymerisations when **1** or **5** were used as catalyst. Lactide polymerisations using salophen complexes **2**-**4** proceeded to high conversions, but had variable molecular weights and polymerisation control. Control was further degraded in *rac-β*BL polymerisations, with high molecular weight polymers observed with complex **4**. This loss of control matches well with deviations previously observed in chromium salophen complexes [2l,5a]. While these deviations were attributed to increase in the viscosity of the polymer melt at high conversions, similar deviations were observed in solution polymerisations [5a] which, coupled with our aluminium results, suggest this may be characteristic of the more rigid salophen ligand framework. In all cases, no effective polymerisation of cyclic ester is observed in the absence of either the aluminium catalyst or alcohol initiator.

Table 1. Polymerisation, Microstructural, and Thermal Data PLA[a] and PHB[b] Polymers

Al	Monomer	% Conv[c]	$M_{n,th}$	M_n[d]	Đ[d]	P_m[e]/P_r[f]	T_g/T_m (°C)
1	*rac*-LA	49	7100	6100	1.07	0.92[g]/-	54/141
2	*rac*-LA	99	14400	14900	1.14	0.47[g]/-	56
3	*rac*-LA	99	14400	17700	1.37	0.45[g]/-	54
4	*rac*-LA	99	14400	23100	1.19	0.46[g]/-	49
5	*rac*-LA	54	7800	6300	1.18	0.93[g]/-	53/162
1	*rac-β*BL	90	7800	6400	1.11	0.54[h]/-	3
2	*rac-β*BL	96	8400	3800	1.39	-/0.54[h]	1
3	*rac-β*BL	88	7700	2300	1.42	-/0.55[h]	−1
4	*rac-β*BL	47	4100	43100	2.21	-/0.53[h]	−6
5	*rac-β*BL	99	8600	6300	1.37	0.55[h]/-	5

[a]Polymerisations were conducted at 70 ˚C in 2 mL toluene with monomer (M):initiator (I):benzyl alcohol (BnOH) ratio of 100:1:1. [b]Polymerisations were conducted at 100 ˚C in 2 mL toluene with M:I:BnOH ratio of 100:1:1. [c]Conversion obtained from ^{1}H NMR spectroscopy. [d]Obtained from GPC. [e]Isotactic enchainment. [f]Syndiotactic enchainment [g]Obtained from ^{1}H{^{1}H} NMR spectra of the CH_3 from C*H* of PLA. [h]Obtained from the ^{13}C NMR spectra of the *C*O of PHB. [i]DSC conducted under nitrogen at a heating rate of 20 ˚C/min and cooling rate of 10 ˚C/min. [j]Melting transition.

Catalysts **2**-**4** produced atactic PLA (Table 1). The lack of isoselectivity of these complexes is likely due to the rigid phenylene backbone that minimizes steric clashes between the growing polymer chain, incoming monomer and the ligand substituents [2p]. No correlation was observed between the finer backbone electronics and stereoselectivity. As expected, the steric bulk of the adamantyl group promotes high isoselectivity in lactide polymerisation, although surprisingly little difference is observed between complexes **1** and **5**. Further, complexes **2**-**4** biased the microstructure of the PHBs towards syndiotacticity (Table 1,

Electronic Supplementary Material, Figures S3-S5). No correlation between the specific electronics of the salophen ligand and tacticity control was found. Interestingly, however, complexes **1** and **5** afforded PHBs with modest isotacticities (P_m = 0.54, 0.55). This suggests that backbone rigidity can play a significant role in tuning catalyst stereoselectivity in these ring-opening polymerisations, as well as suggesting that trends observed may not extend beyond a specific cyclic ester. Of note, chromium salophen initiators have previously been reported to give syndiotactic PHBs under solution polymerisation conditions, although the degree of syndiotactic enchainment (P_r) was not reported [5a].

Kinetic studies on the ROP of *rac*-lactide and *rac*-*β*BL by complexes **1**-**5** also illuminated the intricacies of backbone electronic effects. Previous reports showed a variability in electronic trends: addition of electron-withdrawing groups promoted both marked increases [2l,p,q,5a] and decreases [2o,5b,c,8] in catalytic activity. In our system, apparent rate constants (k_p) were measured through evaluation of monomer conversion and polymer formation by ^{1}H NMR spectroscopy to give $\ln([M]_0/[M]_t)$ vs. time plots with a slope of k_p [2p,q]. Increased electron density at the aluminium centre enhanced k_p in the salophen series (**2** > **3** > **4**, Table 2). This trend was more pronounced in the ROP of *rac*-*β*BL where the overall k_p varied by a factor of 2.2. Very little differences in rates were noted in the salophen-mediated polymerisation of *rac*-LA. Of interest, polymerisation mediated by the salen derivatives **1** and **5** were significantly faster than the salophen catalysts. The homopolymerisation of *β*BL was faster than *rac*-LA for each of these catalysts, in agreement with previous reports [2k], although the difference in monomer preference in copolymerisations remains under investigation.

Interestingly, while linear rates and living polymerisations were observed for the polymerisation of lactide (Figure 3, left), a clear loss of control was observed in the polymerisation of *β*BL by **2**-**4** (Figure 3, right). The non-linearity in monomer consumption is most apparent by a clear shift in polymerisation rate at ca. 5400 s, with ESI-MS data suggesting a competing transesterification reaction may be occurring. These rate data suggest that electronic effects do not play a significant role in controlling rates of polymerisation compared to steric and coordination-sphere effects of an alkyl to aryl backbone switch. Electron-donating groups do increase polymerisation rates slightly, likely due to a decreased electron density at the metal centre increasing lability of metal-alkoxide bonds and promoting acyl bond cleavage. This contrasts with previous reports which suggested that increased electron density at the metal centre results in stronger monomer binding and lower polymerisation rates [8]. Rates do change significantly, and reproducibly (3 repetitions minimum for each catalyst), at the latter stages of *β*BL polymerisation, potentially due to differences in transesterification reactivity.

Table 2. Apparent rates of polymerisation using **1**-**5**.[a]

Initiator	$k_{p,LA}$ ($\times 10^{-6}$ s^{-1})	$k_{p1,\beta BL}$ ($\times 10^{-5}$ s^{-1})	$k_{p2,\beta BL}$ ($\times 10^{-5}$ s^{-1})
1	26.5	33.4	33.5
2	4.91	1.94	2.09
3	4.68	1.79	1.48
4	4.48	1.49	0.945
5	25.2	29.1	28.7

[a] $k_{p,LA}$ = apparent rate of *rac*-LA polymerisation; $k_{p1,\beta BL}$ = apparent initial rate of *rac*-*β*BL polymerisation; $k_{p2,\beta BL}$ = apparent overall rate of *rac*-*β*BL polymerisation.

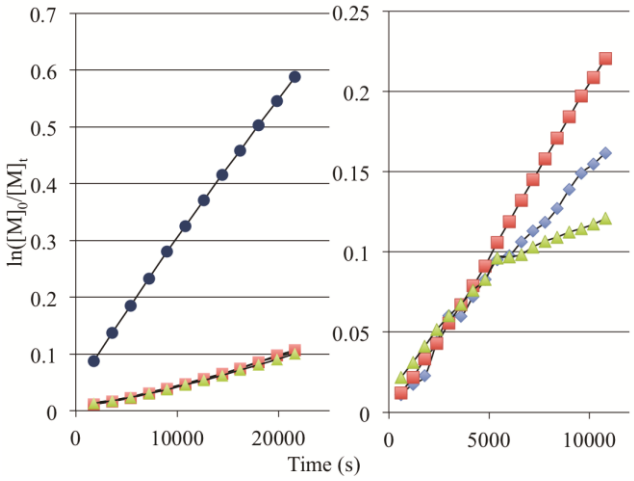


Figure 3. Plot of $\ln[M]_0/[M]_t$ versus time for the ROP of *rac*-*β*BL (right) and *rac*-lactide (left) for catalysts **2** (red square), **3** (blue diamond), **4** (green triangle) and **5** (navy circle).

3. Conclusion

In summary, stereoselectivity of salophen catalysts **2**-**4** was found to be independent of the backbone electronics of the supporting ligand. Though these complexes gave atactic PLAs, they biased the microstructure of PHBs towards syndiotacticity, contrasting the isotactic bias of salen complexes **1** and **5**. Tuning of the backbone electronics of the supporting ligand modulated the efficiency of our salophen complexes in the ROP of *rac*-lactide and *rac*-*β*BL with electron donation on the salophen backbone increasing polymerisation rates. Importantly, salen complexes **1** and **5** offered modest improvements over isoselectivities in cyclic ester polymerisations.

4. Materials and Methods

4.1. General considerations

Manipulations of air- and/or moisture-sensitive compounds were carried out in an MBraun LABmaster sp glovebox. Glassware used in complex synthesis and in polymerisation were dried in an oven at 120 ˚C overnight and subjected to three vacuum-nitrogen cycles before taken into the glovebox. All polymerisation data were obtained in triplicate to ensure reproducibility.

4.2. Materials

All chemicals and solvents were purchased from Sigma-Aldrich unless otherwise stated. *p*-Cresol (99%), tin(IV)chloride (97%), paraformaldehyde powder (95%), *o*-phenylenediamine flaked, (99.5%), 4-methyl-*o*-phenylenediamine (≥ 98%), 4-chloro-*o*-phenylenediamine (97%), 2,2-dimethyl-1.3-propanediamine (99%) and trimethylaluminium (2.0 M solution in heptane) were used without further purification. 1-Adamantanol (99%) was also used as purchased from Alfa Aesar.

Triethylamine (≥ 99%) was dried over calcium hydride at ambient temperature overnight, vacuum transferred and degassed by three freeze-pump-thaw cycles prior to use. Deuterated solvents, obtained from Cambridge Isotope Laboratories, were either dried over 3 Å molecular sieve (chloroform-d (99.8%)) or calcium hydride (benzene-d_6 (D, 99.50%) and toluene-d_8 (D, 99.94%)) at reflux temperature overnight, vacuum transferred and degassed by three freeze-pump-thaw cycles prior to use. Toluene and *n*-pentane, obtained from Caledon Laboratories, Canada, were purified by passing the solvent through an Innovative Technology solvent purification system that consisted of columns of alumina and copper catalyst, and were degassed thrice in a cycle of freeze-pump-thaw prior to use. *rac*-Lactide was obtained from Purac Biomaterials (Gorinchem, The Netherland) and purified by three successive vacuum sublimations. *rac*-*β*-Butyrolactone (≥ 98%) was dried over calcium hydride at ambient temperature overnight, vacuum distilled and degassed thrice by freeze-pump-thaw cycles prior to use.

4.3. Instrumentation

All NMR spectra were acquired on a Bruker Avance NMR spectrometer (^{1}H, 300 MHz and ^{13}C, 75 MHz). Elemental analyses were performed by Guelph Analytical Laboratories. Gel permeation chromatography (GPC) analyses were performed on a Polymer Laboratories PL-GPC 50 Plus integrated GPC system with two 300 × 7.8 mm Jordi Gel DVB mixed bed columns utilising a refractive index detector and a Wyatt Technology miniDAWN™ TREOS® multiple angle light scattering (MALS) detector operating at 658 nm or on a Malvern Instruments Viscotek 270 GPC Max triple detection system with 2× mixed bed styrene/DVB

columns (300 × 7.5 mm). GPC analyses were carried out in HPLC-grade THF at a flow rate of 1 mL/min and at 50 or 35 ˚C. Absolute molecular weights were obtained using dn/dc values of 0.051 mL/g [9] and 0.067 mL/g [10] for poly(lactic acid) (PLA) and poly(3-hydroxybutyrate) (PHB), respectively. Mass spectra were acquired on a Thermo Scientific LTQ Orbitrap Velo high-resolution mass spectrometer fitted with electrospray ionisation source. The spray voltage was operated at 3 kV while the capillary temperature was set at 275 ˚C. Single crystals of **5** were grown from toluene by slow evaporation at ambient temperature. The single crystal was coated with Paratone-N oil, mounted using a polyimide MicroMount and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using MoKα radiation and a graphite monochromator at 173(1) K with 9056 independent reflections giving a final R-index of 0.0507 with graphical interpretations prepared using the ORTEP-3 package [11]. Differential scanning calorimetry (DSC) analyses were conducted under nitrogen using a heat/cool/heat cycle at a heating rate of 20 ˚C and cooling rate of 10 ˚C/min on a TA Instruments DSC Q100 with hermetically sealed aluminium pans.

4.4. General Synthetic Procedures for Ligand Synthesis

Ligands precursors were synthesised via a two-step synthetic approach that involved the prior synthesis of 2-adamantyl-4-phenol [12] and the subsequent conversion of the substituted phenol to 3-adamantyl-5-methylsalicycladehyde [13] based on literature procedures. Ligands were prepared by the condensation reaction of 3-adamantyl-5-methylsalicylaldehyde and the appropriate diamine in a 2:1 stoichiometric ratio in refluxing ethanol (20 mL). The requisite diamine was added to a rapidly stirring ethanolic solution of the salicylaldehyde at ambient temperature and the mixture was heated to reflux temperature for 3 h. The mixture was cooled to ambient temperature, filtered to recover the precipitate, which was dried under vacuum.

4.4.1. Synthesis and Characterisation of N,N'-bis(3-adamantyl-5-methylsalicylidene)-4-methyl-o-phenylenediamine

The ligand was synthesised using 4-methyl-*o*-phenylenediamine following the general procedure outlined above Yield: 0.82 g (39%) ^{1}H NMR data (300 MHz, $CDCl_3$, δ, ppm) 13.49 (s, O*H*, IH), 13.43 (s, O*H*, 1H), 8.58 (s, C*H*=N, 2H), 7.13-7.02 (m, Ar*H*, 7H), 2.42 (s, ArCH_3, 3H), 2.33-1.76 (m, adamantyl *H* and ArCH_3, 36H) ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm) 165.31, 164.56 (Ar*C*=N), 158.95, 158.89 (Ar*C*OH), 142.50, 139.98, 137.88, 137.87, 137.42, 131.81, 131.66, 130.61, 130.50, 127.99, 127.17, 127.15, 121.48, 120.34, 119.13, 119.08 (Ar*C*), 40.42, 37.38, 37.19, 29.33, 21.27, 20.87 (adamantyl *C* and (ArC(*C*H_3)).

4.4.2. Synthesis and Characterisation of N,N'-bis(3-adamantyl-5-methylsalicylidene)-o-phenylenediamin

The ligand was synthesised using *o*-phenylenediamine following the general procedure outlined above. Yield: 0.63 g, (35%) ^{1}H NMR data (300 MHz, $CDCl_3$, δ, ppm) 13.40 (s, O*H*, 2H), 8.59 (s, C*H*=N, 2H), 7.30-7.27 (m, Ar*H*, 2H), 7.23-7.21 (m, Ar*H*, 2H), 7.14 (d, J = 2.1 Hz, Ar*H*, 2H), 7.03 (d, J = 1.5 Hz, Ar*H*, 2H), 2.33-2.30 (m, adamantyl *H*, 6H), 2.16 (d, J = 2.7 Hz) adamantyl *H*, 12H), 2.05 (bs, ArCH_3 6H), 1.81-1.77 (m, adamantyl *H*, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm) 165.38 (Ar*C*=N), 158.97 (Ar*C*OH), 142.68, 137.94, 131.92, 130.61, 127.37, 127.24, 120.70, 119.06 (Ar*C*), 40.41, 37.38, 37.20, 29.32, 20.87 (adamantyl *C* and (ArC(*C*H_3)).

4.4.3. Synthesis and Characterisation of N,N'-bis(3-adamantyl-5-methylsalicylidene)-4-chloro-o-phenylenediamine

The ligand was synthesised using 4-chloro-*o*-phenylenediamine following the general procedure outlined above. Yield: 0.75 g (35%) ^{1}H NMR data (300 MHz, $CDCl_3$, δ, ppm) 13.23 (s, O*H*, 1H), 13.13 (s, O*H*, 1H), 8.57-8.56 (m, C*H*=N, 2H), 2.28 (d, J = 2.4 Hz, Ar*H* 1H), 7.26 (d, J = 2.4 Hz, Ar*H* 1H), 7.21 (d, J = 2.1 Hz, 1H), 7.16-7.13 (m, Ar*H*, 2H), 7.03-7.01 (m, Ar*H*, 2H), 2.34-1.56 (m, adamantyl *H* and ArCH_3, 36H) ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm) 166.08, 165.61 (Ar*C*=N), 159.05, 158.98 (Ar*C*OH), 143.60, 141.33, 138.04, 138.01, 132.52, 132.47, 132.24, 130.82, 130.69, 127.49, 127.41 127.14, 121.71, 120.78, 118.93, 118.84 ((Ar*C*), 40.50, 37.36, 37.21, 29.30, 29.18, 20.86 (adamantyl *C* and (ArC(*C*H_3)).

4.4.4. Synthesis and Characterisation of N,N'-bis(3-adamantyl-5-methylsalicylidene)-2,2-dimethyl-1,3-propanediamine

The ligand was synthesised using 2,2-dimethyl-1,3-propanediamine following the general procedure. Yield: 1.71 g, (83%) ^{1}H NMR data (300 MHz, $CDCl_3$, δ, ppm): 13.81 (s, O*H*, 2H), 8.31 (s, C*H*=N 2H), 7.09 (d, J = 1.8 Hz, Ar*H*, 2H), 6.92 (d, J = 1.5 Hz, Ar*H* 2H), 3.47 (s, NCH_2C(CH_3)$_2$CH_2N 4H) 2.29 (s, adamantyl *H*, 6H), 2.20 (m, adamantyl *H*, 12H), 2.10 (bs, ArCH_3, 6H), 1.86-1.77 (m, adamantyl *H*, 12H), 1.10 (s, $NCH_2C(CH_3)_2CH_2N$, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm) 166.80 (Ar*C*=N), 158.72 (Ar*C*OH), 137.62, 130.60, 129.69, 126.81, 118.57 (Ar*C*), 68.65 (NCH_2C(CH_3)$_2$*C*H_2N), 40.51, 37.41, 37.17, 36.53, 29.35, 24.82, 20.89 (adamantyl *C*, ArC(*C*H_3), $NCH_2C(CH_3)_2CH_2N$, and $NCH_2C(CH_3)_2CH_2N$).

4.5. Synthesis and Characterisation of Aluminium Complexes

4.5.1. Synthesis and Characterisation of ^{Me}[salophen]AlMe, ***2***

A solution of trimethlyaluminium (0.49 mL, 1.0 mmol) in heptane was slowly added to a vigorously stirred toluene (20 mL) solution of *N,N'*-bis(3-adamantyl-5-methylsalicylidene)-4-methyl-*o*-phenylenediamine (0.60 g, 1.0 mmol) under inert atmosphere. The mixture was refluxed for 12 h, cooled to ambient temperature and filtered to recover the precipitate. The precipitate was washed with *n*-pentane and dried under vacuum. Yield: 0.33 g, (50%). ^{1}H NMR data (300 MHz, $CDCl_3$, δ, ppm) 7.94 (s, C*H*=N, 1H), 7.90 (s, C*H*=N, 1H), 7.33 (d, J = 2.1 Hz, Ar*H*, 2H) 6.70, 6.65, 6.58 Ar*H*, 5H), 2.52 (t, J = 11.4 Hz, 12 Hz, adamantyl H, 12*H*), 2.26 (s, adamantyl *H*, 6H), 2.18 (ArC(CH_3)), 1.98 (t, J = 10.2 Hz, 11.7 Hz, adamantyl *H*, 6H), 1.81 (d, J = 11.7 Hz, adamantyl *H*), –0.32 (s, AlCH_3, 3H). ^{13}C NMR (75 MHz, C_6H_6, δ, ppm) 166.02, 165.98 (*C*=N), 160.97, 160.34 (Ar*C*OH), 142.31, 142.27, 139.65, 138.11, 137.51, 136.21, 136.02, 131.95, 131.88, 129.69, 125.25, 120.85, 117.07, 116.14 (Ar*C*), 41.51, 38.28, 38.02, 30.13, 21.09 (adamantyl *C*, and ArC(*C*H_3)). Anal. Calcd (found) for $C_{44}H_{51}AlN_2O_2$: C, 79.25 (78.88); H, 7.71 (7.50); Al, 4.05 (3.92); N, 4.20 (4.11); O, 4.80 (4.74).

4.5.2. Synthesis and Characterisation of ^{H}[salophen]AlMe, ***3***

In an analogous procedure to the synthesis of **2**, *N,N'*-bis(3-adamantyl-5-methylsalicylidene)-*o*-phenylenediamine was used to prepare complex **3**. Yield: 0.44 g, (68%). ^{1}H NMR data (300 MHz, $CDCl_3$, δ, ppm) 7.89 (s, C*H*=N, 2H), 7.34 (d, J = 2.4 Hz, Ar*H*, 2H), 6.83 (m, Ar*H*, 2H), 6.72 (m, Ar*H*, 2H), 6.61 (s, Ar*H*, 2H), 2.51 (bs, adamantyl *H*, 12H), 2.25 (bs, ArC(CH_3)), 6H), 2.14 (d, J = 15.3 Hz, adamantyl *H*, 6H), 1.94 (d, J = 11.7 Hz, adamantyl *H*, 6H), 1.80 (d, J = 11.7 Hz, adamantyl *H*, 6H), –0.33 (s, AlCH_3, 3H) ^{13}C NMR (75 MHz, C_6H_6, δ, ppm) 166.25 (*C*=N), 161.00 (Ar*C*OH), 142.28, 139.71, 136.25, 131.86, 129.89, 125.23, 120.68, 116.33 (Ar*C*–N), 41.39, 38.18, 37.91, 30.03, 20.98 (adamantyl *C* and ArC(*C*H_3)). Anal. Calcd (found) for $C_{43}H_{49}AlN_2O_2$: C, 79.11 (79.14); H, 7.57 (7.33); Al, 4.13 (4.40); N, 4.29 (4.38); O, 4.90 (4.59).

4.5.3. Synthesis and Characterisation of ^{Cl}[salophen]AlMe, ***4***

In an analogous procedure to the synthesis of **2**, *N,N'*-bis(3-adamantyl-5-methylsalicylidene)-4-chloro-*o*-phenylenediamine was used to prepare complex **4**. Yield: 0.32 g, (48%). ^{1}H NMR data (300 MHz, $CDCl_3$, δ, ppm) 7.74 (s, C*H*=N, 1H), 7.57 (s, C*H*=N, 1H), 7.32 (d, J = 1.8 Hz, Ar*H*, 2H), 6.81 (d, J = 6.9 Hz, Ar*H*), 6.59, 6.52, (s, Ar*H*, 2H), 6.40 (d, J = 9.3 Hz, Ar*H*, 1H), 2.48 (bs, adamantyl *H*, 12H), 2.24 (s, adamantyl *H*, 6H), 2.11 (s, ArC(CH_3), 6H), 1.93 (d, J = 11.7 Hz, adamantyl *H*, 6H), 1.79 (d, J = 11.4 Hz, adamantyl *H*, 6H), –0.38 (s, AlCH_3). ^{13}C NMR (75 MHz, C_6H_6, δ, ppm) 166.65, 166.61 (*C*=N), 162.83, 162.78 (Ar*C*OH), 142.42, 140.58, 138.35, 136.93, 136.68, 133.51, 132.28, 131.94, 129.69, 126.06, 125.53, 120.70, 120.63, 117.57,

117.03 (Ar*C*), 41.43, 38.25, 37.96, 30.08, 21.01 (adamantyl *C*, and ArC(CH_3)). Anal. Calcd (found) for $C_{43}H_{48}AlClN_2O_2$: C, 75.15 (75.32); H, 7.04 (6.87); Al, 3.93 (3.65); Cl, 5.16 (4.89), N, 4.08 (4.32); O, 4.66 (4.91).

4.5.4. Synthesis and Characterisation of DMP[salophen]AlMe, 5

In an analogous procedure to the synthesis of **2**, *N,N'*-bis(3-adamantyl-5-methylsalicylidene)-2,2-dimethyl-1,3-propanediamine was used. Yield: 0.31 g, (49%). ^{1}H NMR data (300 MHz, C_6H_6, δ, ppm) 7.39 (s, C*H*=N, 2H), 7.33 (d, J = 2.1 Hz, Ar*H*, 2H), 6.64 (s, Ar*H*, 2H), 2.99 (d, J = 12 Hz, NC*H*HC(CH_3)$_2$C*H*HN, 2H), 2.67 (d, J = 12 Hz, NCH*H*C(CH_3)$_2$CH*H*N, 2H), 2.50 (t, J = 15.6 Hz, adamantyl *H*, 12H), 2.29, (bs, ArC(CH_3), 6H), 2.14 (d, J = 16.2 Hz, adamantyl H, 6H), 1.90 (d, J = 11.7 Hz, adamantyl *H*, 6H), 1.78 (d, J = 12 Hz, adamantyl *H*, 6H), 0.52, 0.37 (s, NCHHC(CH_3)$_2$CHHN, 6H), –0.31 (s, AlCH_3, 3H). ^{13}C NMR (75 MHz, C_6H_6, δ, ppm) 169.16 (Ar*C*=N), 164.89 (Ar*C*OH), 142.11, 134.94, 131.57, 129.70, 124.63, 120.21 (Ar*C*), 68.17 (N*C*H$_2$C(CH_3)$_2$*C*H$_2$N), 41.39, 38.18, 37.95, 35.91, 30.15, 25.31, 25.10 (adamantyl *C*, N*C*H$_2$*C*(CH_3)*C*H$_2$N, N*C*H$_2$C(*C*H$_3$)$_2$*C*H$_2$N, and ArC(*C*H$_3$)). Anal. Calcd (found) for $C_{42}H_{55}AlN_2O_2$: C, 77.98 (78.19); H, 8.57 (8.54); Al, 4.17 (3.89); N, 4.33 (4.14); O, 4.95 (5.18).

4.6. General Polymerisation Procedures

4.6.1. Polymerisation of rac-Lactide

A mixture of the desired aluminium complex (0.02 mmol), benzyl alcohol (2.1 μL, 0.02 mmol) and *rac*-lactide (288 mg, 2 mmol) in toluene (2 mL) was prepared in a glovebox in a Kontes ampoule and sealed under nitrogen. The reaction was heated at 70 ˚C under vigorous stirring until conversion exceeded 90% or the requisite time had expired (8h). The reaction was quenched with a drop of methanol and the polymer was precipitated from excess cold methanol. The polymer was dried under vacuum at ambient temperature.

4.6.2. Polymerisation of rac-β-Butyrolactone

A mixture of the desired aluminium complex (0.03 mmol), benzyl alcohol (3.1 μL, 0.03 mmol) and *rac-β*-butyrolactone (258 mg, 3 mmol) in toluene (2 mL) was prepared in a glovebox in a Kontes ampoule and sealed under nitrogen. The reaction was heated at 100 ˚C for 24 h (complexes **2**-**4**) or 3 h (complex **5**). The mixture was quenched with methanol, cooled to ambient temperature and the polymer precipitated from Et_2O/*n*-hexane 1:3 mixture. The isolated polymer was dried under vacuum at ambient temperature.

4.6.3. Kinetic Analyses of Polymerisations

Polymerisations were conducted in sealed Young's tap NMR tubes under nitrogen atmosphere. The polymerisations of *rac*-lactide were conducted in benzene-d_6 at 70˚C while those of *rac*-*β*-butyrolactone were conducted in toluene-d_8 at 100 ˚C. The molar ratio of monomer to initiator was fixed at 50:1 in each instance. In a 300 MHz NMR spectrometer fixed at the aforementioned temperature, the monomer conversion and polymer formation were determined by ^{1}H NMR spectroscopy.

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